

April 15, 2004  
Page 3

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

**AMENDMENTS TO THE CLAIMS:**

Please amend the claims as indicated below:

1. -- 2. (Canceled)
3. (Previously presented) A method of degrading a predetermined substrate used for hydrocarbon exploitation comprising:  
providing a fluid or a solid, or a mixture thereof, containing a substrate-degrading agent inactivated by encapsulation, said inactivated substrate-degrading agent initially being substantially inactive, and subsequently becoming active in response to a predetermined triggering signal; and  
applying the triggering signal to said fluid or solid or mixture thereof such that said substrate-degrading agent becomes activated, the activated substrate-degrading agent being capable of at least partially degrading the substrate, said triggering signal selected from the group consisting of exposure to a reducing agent, oxidizer, chelating agent, radical initiator, carbonic acid, ozone, chlorine, bromine, peroxide, electric current, ultrasound, change in pH, change in salinity, change in ion concentration, reversal of wellbore pressure-differential, and combinations thereof.
4. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to a change in pH environment.
5. (Previously presented) The method of claim 4 wherein said step of exposing the inactivated substrate-degrading agent to a change in pH comprises lowering the pH environment.
6. (Previously presented) The method of claim 5 wherein said step of lowering the pH environment comprises exposing the inactivated substrate-degrading agent to carbonic acid.
7. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to a change in salinity.

April 15, 2004  
Page 4

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

8. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to a reducing agent.
9. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to an oxidizer.
10. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to a chelating agent.
11. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to a radical initiator.
12. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to ozone.
13. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to chlorine or bromine.
14. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to peroxide.
15. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to an electric current.
16. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to ultrasound.

April 15, 2004  
Page 5

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

17. (Previously presented) The method of claim 3 wherein said step of applying a triggering signal comprises exposing the inactivated substrate-degrading agent to a change in ion concentration.

18. (Canceled)

19. (Previously presented) The method of claim 3 comprising exposing the inactivated substrate-degrading agent to a reversal of wellbore pressure-differential.

20. (Previously presented) The method of claim 3 wherein said substrate-degrading agent comprises at least one agent chosen from the group consisting of enzymes, microorganisms, spores and inorganic chemicals.

21. (Previously presented) The method of claim 3 wherein said encapsulation comprises encapsulating said substrate-degrading agent with an encapsulating material that maintains the substrate-degrading agent substantially inactive initially, and is responsive to said triggering signal such that at least a portion of said substrate-degrading agent is released by said encapsulating material upon exposure to said triggering signal.

22. (Previously presented) The method of claim 3 wherein said encapsulating material is formed of a co-polymer of (a) an ethylenically unsaturated hydrophobic monomer with (b) a free base monomer of the formula



where R is hydrogen or methyl, R<sup>2</sup> is alkylene containing at least two carbon atoms, X is O or NH, R<sup>3</sup> is a hydrocarbon group containing at least 4 carbon atoms and R<sup>4</sup> is hydrogen or a hydrocarbon group.

April 15, 2004  
Page 6

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

23. (Original) The method of claim 22 wherein  $R^3$  is t-butyl and  $R^4$  is hydrogen.
24. (Previously presented) The method of claim 22 wherein  $R^1$  is methyl,  $R^2$  is ethylene and X is O.
25. (Original) The method of claim 22 wherein the hydrophobic monomer is a styrene or methylmethacrylate.
26. (Original) The method of claim 22 wherein said encapsulating material is a co-polymer of styrene or methyl methacrylate with t-butyl amino ethyl methacrylate.
27. (Original) The method of claim 22 wherein said co-polymer is 55 to 80 weight% styrene, methyl styrene or methyl methacrylate with 20 to 45 weight% t-butylamino-ethyl methacrylate.
- 28-29. (Canceled)
30. (Previously presented) The method of claim 21 wherein the fluid or solid comprises at least two inactivated substrate-degrading agents, each of which is inactivated by encapsulation, wherein the inactivated substrate-degrading agents are capable of being activated by the same or different triggering signals, such that upon activation the activated substrate-degrading agents are capable of acting upon the same or different substrates independently or in concert.
31. (Previously presented) The method of claim 20 wherein said substrate-degrading agent comprises an endo-amylase.
32. (Previously presented) The method of claim 20 wherein said substrate-degrading agent is alpha-amylase.

April 15, 2004  
Page 7

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

33. (Previously presented) The method of claim 20 wherein said substrate-degrading agent comprises at least one enzyme selected from the group consisting of exo-amylases, isoamylases, glucosidases, amylo-glucosidases, malto-hydrolases, maltosidases, isomalto-hydrolases and malto-hexaosidases.

34. (Previously presented) The method of claim 20 wherein the released substrate-degrading agent is capable of being deactivated by application of a second triggering signal, wherein the second triggering signal may be the same or a different triggering signal, such that the deactivated substrate-degrading agent no longer acts on the substrate.

35. (Previously presented) The method of claim 3 wherein the degradable substrate is selected from the group consisting of celluloses, derivatized celluloses, starches, derivatized starches, xanthans and derivatized xanthans.

36. (Previously presented) The method of claim 3 wherein the fluid is chosen from the group consisting of circulating drilling fluid, completion fluid, stimulation fluid, gravel packing fluid and workover fluid.

37. (Previously presented) The method of claim 3 wherein the fluid is a fracturing fluid.

38. (Canceled)

39. (Previously presented) The method of claim 3 wherein said solid comprises a device or particle suitable for use downhole or on the surface for hydrocarbon exploitation.

40. (Previously presented) A method of increasing the flow of hydrocarbons from a well, the method comprising:

April 15, 2004  
Page 8

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

providing a fluid comprising a degradable polymeric substrate and a substrate-degrading agent inactivated by encapsulation, said inactivated substrate-degrading agent being substantially inactive initially, and becoming active in response to a predetermined triggering signal;

introducing the fluid into a downhole environment; and,

applying the triggering signal, the triggering signal being sufficient to activate the inactivated substrate-degrading agent to give an activated substrate-degrading agent,

the activated substrate-degrading agent being capable of selectively degrading the substrate sufficient to alter a physical property of the fluid or a solid formed therefrom such that the flow of hydrocarbons from said well is increased, wherein said triggering signal is chosen from the group consisting of reducing agent, oxidizer, chelating agent, radical initiator, carbonic acid, ozone, chlorine, bromine, peroxide, electric current, ultrasound, change in pH, change in salinity, change in ion concentration, reversal of wellbore pressure-differential, and combinations thereof.

41. (Previously presented) The method of claim 40 comprising:

carrying out drilling activity wherein said fluid comprises a circulating drilling fluid containing the polymeric substrate and the inactivated substrate-degrading agent, wherein the agent comprises an inactivated enzyme that is capable of withstanding the dynamic environmental conditions generated while drilling; and

forming a low-permeability filter cake or fluid invasion zone containing said degradable polymeric substrate and said inactivated enzyme, said low-permeability filter cake or fluid invasion zone retaining low-permeability until receipt of said triggering signal sufficient to activate at least a portion of said enzyme.

42. (Previously presented) The method of claim 40 wherein the agent comprises more than one inactivated enzyme, wherein the inactivated enzymes are capable of being activated by the same or different triggering signals, wherein upon activation the activated enzymes are capable of acting upon the same or different substrates.

April 15, 2004  
Page 9

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

43. (Previously presented) The method of claim 40 wherein the fluid is chosen from the group consisting of a circulating drilling fluid, a completion fluid, a workover fluid, a fracturing fluid, a gravel packing fluid and a stimulation fluid.

44. (Canceled)

45. (Currently Amended) ~~The method of claim 44 further comprising~~ A method of degrading filter cake, the method comprising:

providing a fluid comprising a polymeric viscosifier or fluid loss control agent and an enzyme inactivated by sequestration, said inactivated enzyme being responsive to a predetermined triggering signal;

introducing the fluid into a downhole environment such that a filter cake containing said polymeric viscosifier or fluid loss control agent and said inactivated enzyme is formed;

applying the triggering signal selected from the group consisting reducing agent, oxidizer, chelating agent, radical initiator, carbonic acid, ozone, chlorine, bromine, peroxide, electric current, ultrasound, change in salinity, change in pH, change in ion concentration, reversal of wellbore pressure-differential, and combinations thereof, to activate the inactivated enzyme to give an activated enzyme, the activated enzyme being capable of selectively degrading said polymeric viscosifier or fluid loss control agent such that said filter cake containing said viscosifier or fluid loss control agent at least partially disintegrates, and

dislodging a piece of drilling equipment from said at least partially disintegrated filter cake.

46. - 48 (Canceled)

April 15, 2004  
Page 10

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

49. (Previously presented) A wellbore treatment method comprising:

providing a fluid or a solid, or mixture thereof, containing a substrate-degrading agent inactivated by sequestration, said inactivated substrate-degrading agent being responsive to a predetermined triggering signal such that said substrate-degrading agent becomes activated upon exposure to said triggering signal, the activated substrate-degrading agent being capable of degrading a previously existing downhole substrate;

introducing said fluid or solid, or mixture thereof, into a downhole environment that contains said substrate; providing said triggering signal selected from the group consisting of exposure to a reducing agent, oxidizer, chelating agent, radical initiator, carbonic acid, ozone, chlorine, bromine, peroxide, electric current, ultrasound, change in salinity, change in pH, change in ion concentration, reversal of wellbore pressure-differential, and combinations thereof, to activate the substrate-degrading agent; and

allowing the substrate-degrading agent to at least partially degrade the substrate.

50-85. (Canceled)

86. (Previously presented) The method of claim 3 comprising allowing said substrate to at least partially degrade.

87. (Previously presented) The method of claim 3 comprising initial conditions of use of said fluid or solid or mixture thereof, and subsequent conditions of use of said fluid or solid or mixture thereof resulting from said applying said triggering signal.

88. (Previously presented) The method of claim 3 wherein said fluid or solid or mixture thereof contains said degradable substrate.



April 15, 2004  
Page 11

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

89. (Previously presented) The method of claim 88 wherein said solid comprises a filter cake or a bridging particle.

90. (Previously presented) The method of claim 88 comprising allowing said substrate to degrade whereby a physical property of said fluid or solid is altered, said triggering signal being incapable of effecting said alteration if applied in the absence of said inactivated substrate-degrading agent.

91. (Previously presented) The method of claim 5 wherein said step of lowering the pH environment comprises reducing the pressure within an excavation so that naturally-occurring carbonic acid, hydrosulfuric acid, or other naturally occurring acid or precursors thereof, previously excluded from said excavation by application of higher pressure, enter into said excavation to lower the pH environment of the inactivated substrate-degrading agent.

92. (Canceled)

93. (Previously presented) The method of claim 3 wherein said inactivated substrate-degrading agent is separate from said substrate and said method comprises:

supplying said triggering signal to said fluid or solid or mixture thereof containing said inactivated substrate-degrading agent such that said substrate-degrading agent becomes activated; and

exposing said activated substrate-degrading agent to said substrate.

94. (Previously presented) The method of claim 3 wherein said inactivated substrate-degrading agent comprises particles up to about 74 microns in diameter.

April 15, 2004  
Page 12

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

95. (Previously presented) The method of claim 3 wherein said inactivated substrate-degrading agent is capable of withstanding shear forces generated during drilling.

96. (Previously presented) The method of claim 3 wherein said inactivated substrate-degrading agent is capable of withstanding dynamic exposure to drilling temperatures.

97. (Previously presented) The method of claim 96 wherein said inactivated substrate-degrading agent is capable of withstanding dynamic exposure to temperatures up to 200°F.

98. (Canceled)

99. (Currently amended) A method of degrading a predetermined substrate used for hydrocarbon exploitation comprising:

providing a fluid or a solid, or a mixture thereof, containing a substrate-degrading agent inactivated by sequestration, said inactivated substrate-degrading agent initially being substantially inactive, and subsequently becoming active in response to a predetermined triggering signal; and

applying said triggering signal to said fluid or solid or mixture thereof such that said substrate-degrading agent becomes activated, the activated substrate-degrading agent being capable of at least partially degrading the substrate, wherein said triggering signal is selected from the group consisting of exposure to a reducing agent, oxidizer, chelating agent, radical initiator, carbonic acid, ozone, chlorine, bromine, peroxide, electric current, ultrasound, change in salinity, change in pH, change in ion concentration, reversal of wellbore pressure-differential, and combinations thereof, and

wherein said substrate-degrading agent is chosen from the group consisting of enzymes, microorganisms, spores, oxidizers and acids, and

wherein said acid is derived from a neutral polymer.

April 15, 2004  
Page 13

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

100. (Previously presented) The method of claim 99 wherein said neutral polymer is polyhydroxyacetic acid.

101. (Previously presented) The method of claim 4 wherein said inactivated substrate-degrading agent comprises an encapsulating material that becomes permeable to said substrate-degrading agent after exposure to said pH change, and said method comprises applying said pH change whereby said substrate-degrading agent passes through said encapsulating material.

102. (Previously presented) A method of increasing the permeability of filter cake in a wellbore, the method comprising:

obtaining a polymeric viscosifier or fluid loss control agent and a breaking agent capable of degrading said polymeric viscosifier or fluid loss control agent;

encapsulating said breaking agent in an ionophoric encapsulating material to obtain an encapsulated breaking agent, said ionophoric encapsulating material being impermeable to said breaking agent at a defined first pH and permeable to said breaking agent at a defined second pH;

carrying out drilling activity whereby a filter cake is formed comprising said polymeric viscosifier or fluid loss control agent and said encapsulated breaking agent, said filter cake having a first permeability to a defined wellbore fluid;

changing the pH of the filter cake from said first pH to said second pH, whereby permeability of said encapsulating material to said breaking agent changes such that said breaking agent becomes unencapsulated;

allowing said unencapsulated breaking agent to at least partially degrade said polymeric viscosifier or fluid loss control agent such that the permeability of said filter cake changes from said first permeability to a second permeability that is greater than said first permeability.

April 15, 2004  
Page 14

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

103. (Previously presented) The method of claim 49 comprising removing drilling fluid from said downhole environment before applying said triggering signal.

104. (Previously presented) The method of claim 3 further comprising exposing the inactivated substrate-degrading agent to a change in pressure and/or temperature.

105. (Canceled)

106. (Previously presented) The method of claim 39 wherein the solid comprises a perforation gun holder or a film sheath for a sand screen assembly.

107. (Canceled)

108. (Previously presented) The method of claim 40 further comprising exposing said inactivated substrate-degrading agent to a change in pressure and/or temperature.

109. (Previously presented) The method of claim 40 wherein applying said triggering signal comprises exposing said inactivated substrate-degrading agent to a downhole reversal of wellbore pressure-differential.

110. (Previously presented) The method of claim 40 wherein said substrate-degrading agent comprises at least one enzyme.

111. (Previously presented) The method of claim 40 wherein said fluid comprises a drilling fluid.

112. - 115. (Canceled)

April 15, 2004  
Page 15

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

116. (Previously presented) The method of claim 49 further comprising exposing said inactivated degrading agent to a change in pressure.

117. (Previously presented) The method of claim 49 further comprising exposing said inactivated degrading agent to a change in temperature.

118. (Previously presented) The method of claim 49 wherein said sequestration comprises encapsulation of said degrading agent.

119. (Previously presented) The method of claim 49 wherein said degrading agent comprises at least one enzyme.

120. (Previously presented) The method of claim 49 wherein said fluid comprises a drilling fluid.

121. (Previously presented) The method of claim 102 wherein said breaking agent comprises at least one enzyme.

122. (Previously presented) The method of claim 22 wherein the fluid is chosen from the group consisting of a circulating drilling fluid, a completion fluid, a workover fluid, a fracturing fluid, a gravel packing fluid and a stimulation fluid.

123. (Previously presented) The method of claim 22 wherein said solid comprises a device or particle suitable for use downhole or on the surface for hydrocarbon exploitation.

124. (Previously presented) The method of claim 123 wherein said solid comprises a filter cake or a bridging particle.

April 15, 2004  
Page 16

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

125. - 130 (Canceled)

131. (Previously presented) The method of claim 109 wherein said downhole reversal of wellbore pressure-differential causes the release of CO<sub>2</sub> in the downhole environment which causes a change in pH.

132. (Previously presented) The method of claim 3 wherein said encapsulated substrate-degrading agent is capable of responding to said triggering signal such that said agent becomes sufficiently unencapsulated to allow said agent to degrade the substrate.

133. - 148 (Canceled)

149. (Currently Amended) ~~The method of claim 148~~ A method of degrading a predetermined substrate used for hydrocarbon exploitation comprising:

providing a fluid or a solid, or a mixture thereof, containing a substrate-degrading agent inactivated by sequestration, said inactivated substrate-degrading agent initially being substantially inactive, and subsequently becoming active in response to a predetermined triggering signal; and

applying said triggering signal to said fluid or solid or mixture thereof such that said substrate-degrading agent becomes activated, the activated substrate-degrading agent being capable of at least partially degrading the substrate, wherein said triggering signal is selected from the group consisting of exposure to a reducing agent, oxidizer, chelating agent, radical initiator, carbonic acid, ozone, chlorine, bromine, peroxide, electric current, ultrasound, change in salinity, change in pH, change in ion concentration, reversal of wellbore pressure-differential, and combinations thereof, and

exposing the inactivated substrate-degrading agent to a change in pH environment, and wherein exposing the inactivated substrate-degrading agent to a change in pH comprises lowering the pH environment, and

April 15, 2004  
Page 17

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

wherein lowering the pH environment comprises exposing the inactivated substrate-degrading agent to carbonic acid.

150. (Previously presented) The method of claim 102 wherein said encapsulating material is formed of a co-polymer of (a) an ethylenically unsaturated hydrophobic monomer with (b) a free base monomer of the formula



where R is hydrogen or methyl, R<sup>2</sup> is alkylene containing at least two carbon atoms, X is O or NH, R<sup>3</sup> is a hydrocarbon group containing at least 4 carbon atoms and R<sup>4</sup> is hydrogen or a hydrocarbon group.

151. (Previously presented) The method of claim 150 wherein R<sup>3</sup> is t-butyl and R<sup>4</sup> is hydrogen.

152. (Previously presented) The method of claim 150 wherein R<sup>1</sup> is methyl, R<sup>2</sup> is ethylene and X is O.

153. (Previously presented) The method of claim 150 wherein the hydrophobic monomer is a styrene or methylmethacrylate.

154. (Previously presented) The method of claim 150 wherein said encapsulating material is a co-polymer of styrene or methyl methacrylate with t-butyl amino ethyl methacrylate.

155. (Previously presented) The method of claim 150 wherein said co-polymer is 55 to 80 weight% styrene, methyl styrene or methyl methacrylate with 20 to 45 weight% t-butylamino-ethyl methacrylate.

156. (Canceled)

April 15, 2004  
Page 18

Serial No.: 09/711655  
Confirmation No.: 7877  
Applicant: FREEMAN  
Atty. Ref.: PA-00083US

157. (Previously presented) The method of claim 3 wherein said substrate-degrading agent inactivated by encapsulation is prepared prior to containment in said fluid, solid or mixture thereof.

158. (Previously presented) The method of claim 40 wherein said substrate-degrading agent inactivated by encapsulation is prepared prior to containment in said fluid.

159. (Canceled)

160. (Previously presented) The method of claim 46 wherein said degrading agent inactivated by encapsulation is prepared prior to containment in said fluid.

161. (Previously presented) The method of claim 49 wherein said substrate-degrading agent inactivated by encapsulation is prepared prior to containment in said fluid, solid or mixture thereof.

162. (Previously presented) The method of claim 102 comprising combining said encapsulated breaking agent and said polymeric viscosifier or fluid loss control agent in a drilling fluid.

163. (Canceled)